ANL-FNAL SRF CAVITY SURFACE TREATMENT FACILITY. AIR POLLUTION ISSUES

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Buffered Chemical Polishing uses a mix of acids to remove a layer of Nb. The most common acid mix is prepared using hydrofluoric, nitric, and phosphoric acids:

1 volume part of Hydrofluoric Acid (49% wt HF),
1 volume part of Nitric Acid (69.5% wt HNO_3),
2 volume parts of Phosphoric Acid (85% wt H_3PO_4)

Main chemical reactions:

One of the basic reactions in chemistry is the one that starting from one metal and one acid generates salts. In the case of Nb reacting with HNO_3 the result is different due to the generation of niobium oxide that can be removed from the metal surface using HF. This phenomenon allows controlling the reaction speed and heat generation since the oxide film act as inhibitor of the primary reaction. In addition, a third acid, H_3PO_4, serves as a buffer during the process. H_3PO_4 itself doesn't react directly with the metal but balances the H^+ concentration in the solution. The reactions during the process are:

1. Reaction of Nb with nitric acid HNO_3 results in forming a protective level of Nb_2O_5 :

$2Nb + 10HNO_3 => Nb_2O_5 + 10NO_2 + 5H_2O$

2. The niobium oxide reacts with HF to form niobium fluorite salt NbF_5:

$Nb_2O_5 + 10HF => 2NbF_5 + 5H_2O$

3. Orthophosphoric acid H_3PO_4 serves as a buffer that helps to keep reaction rate at a constant level providing a source of H^+ ions to the solution.

$H_3PO_4 <--> H^+ + H_2PO_4^-$

NO_2 release

For each mole of Nb, five moles of NO_2 evolve.
The maximum surface of Nb exposed to acid is about 14 ft^2 (for a TESLA-type cavity). The maximum etching depth for one etching cycle is about 0.004 inches. This results in a total volume of Nb of 8.0 in^3 or 2.5 lbs that corresponds to 12 moles. According to the chemical equation (1), five moles of NO_2 will evolve for each mole of Nb etched out, or totally 60 moles (6.1 lbs). Taking into account an etching rate of about 0.00004 in/min at 59 F, the total etching cycle will take 100 minutes, and gas release rate will be about **3.6 lbs/h**. The total (maximum) amount of NO_2 released during the process is 6.1 lbs.

Mists

There are also mists of hydrofluoric and nitric acids that evolve during the procedure. The evaporation rates were calculated using of the Evaporation Calculator available from the web site:
http://response.restoration.noaa.gov/cameo/evapcalc/evap.html#.
The amount of mist released during the process varies depending on the stage of the process. It depends also on the process temperature and ventilation condition.

Taking into account that the minimum velocity of air for local tank ventilation is 100 – 150 cfm/sq.ft. of open acid surface, we will accept with some reserve, 200 fpm wind speed while calculating evaporation rates. The temperature of the acid mix during the BCP process is accepted on the level of its maximum limit of 68 F.
The concentration of acids is based on their content in the mix. For HF it is 12.5%, for HNO_3 it is 17.5%.

For HF one obtains an evaporation rate of 0.00125 lbs/h per 1 sqft of open acid surface. With a maximum tank size of 12 sqft, we get **0.015 lbs/hour**.
For HNO_3 we have an evaporation rate of 0.002 lbs/h per 1 sqft of open acid surface, which results in the integrated rate of **0.023 lbs/hour.**

EP process

The principle of electrolytic cells is used to remove the superficial layer on Niobium cavities. In this case an electrical potential is applied between a cathode and an anode to obtain the reaction. Electropolishing uses an electrolyte solution that contains 89.5% by volume sulfuric acid H_2SO_4 (96% concentrated by weight) and 10.5% by volume hydrofluoric acid HF (40% concentrated by weight). A constant acid flow rate of about 15 GPM is used. Electric current density used is about 50 mA/cm^2. The surface of a Nb cavity serves as an anode, and an inert cathode is made of Al. The process temperature is about 86 F.

The reactions at the anode are:

$2\ Nb + 5\ H_2O \Rightarrow Nb_2O_5 + 10\ H^+ + 10\ e^-$
$2\ H_2O \Rightarrow O_2 + 4\ H^+ + 4\ e^-$

The reaction at the cathode is:

$2\ H^+ + 2e^- \Rightarrow H_2$

H_2SO_4 serves as electrolyte, and HF allows the removal of the niobium oxide from the surface of the anode.
The only gas evolved is molecular hydrogen, which is removed by the ventilating system.
The amount of fumes released during the process is estimated using the same approach used for the BCP. The same tank area and wind speed are used, but the process temperature and acid concentrations are different.
For HF we get a concentration 4% and an emission rate of 0.00062 lbs/h per 1 sq. ft of acid surface. This results in 0.0075 lbs/h of integrated emission rate.
For sulfuric acid H_2SO_4 concentration is 86% and emission rate is $1\cdot10^{-7}$ lbs/h per 1 sq. ft of acid surface. This results in $1\cdot10^{-6}$ lbs/h of integrated emission rate.
Table 1 summarizes the results taking into account that only one BCP or EP process takes place at any time.

Table 1. Fume generation

Acid	NO_2	HF	HNO_3	H_2SO_4
Solution temperature (F)	68	68 (BCP) 86 (EP)	68	86
Evaporation rate	3.6 (BCP)	0.015 (BCP)	0.023 (BCP)	$1\cdot10^{-6}$ (EP)

(lbs/h)		0.0075 (EP)		

Failure mode

In case of spill, acid is removed from the etching tank followed by filling it with DI water, so that NO_2 generation stops. There are two scenarios to treat acid spill in the process rooms. First, each barrel or tank can be placed in a secondary container. If spill is confined within this container, no major increase of acid fumes generation is expected. When a major acid leak cannot be confined within the secondary containers, it will be collected in the room sump with a significant increase of the acid wetted area (drops of acid and wetted surfaces). The surface increase factor can reach 10, so fume generation rate will increase correspondingly. Pumping acid out of the sump and rinsing the sump and wetted surfaces will significantly reduce fume generation.

Typical and Maximum Hours of Operation

Table 3 provides an estimate of hours of operation and annual emissions for the BCP process. It is accepted that the process of NO_2 releasing lasts for 2 hours, but other pollutants can evolve for 10 hours (in the case of manual etching of small parts in preparation for cavity assembly). Only one BCP cycle a day in each room can take place. During the initial stage (normal operation) only one cycle a week is considered. The maximum load possible (mass production) corresponds to a daily cycles configuration.

Table 3. Annual emission of fumes (BCP) for one room

Pollutant	NO_2	HF	HNO_3
Gas release rate (lbs/h)	3.6	0.015	0.023
Hours per day per cycle (h)	2	10	10
Days per week (normal)	1	1	1
Days per week (maximum)	5	5	5
Weeks per year	50	50	50
Emission per year (normal (lbs/year)	360	7.5	11.5
Emission per year (maximum) (lbs/year)	1800	37.5	57.5

Table 4 provides an estimate of hours of operation and annual emissions for the EP process. It is accepted that the pollutants can evolve for 10 hours. Only one EP cycle a day in each room can take place. During the initial stage (normal operation) only one cycle a week is considered and only in one room. The maximum load possible (mass production) corresponds to a daily cycles configuration in both rooms.

Table 4. Annual emission of fumes (EP) for one room

Pollutant	HF	H_2SO_4
Gas release rate (lbs/h)	0.0075	$1 \cdot 10^{-6}$
Hours per day per cycle (normal) (h)	10	10
Hours per day per cycle (maximum) (h)	10	10
Days per week (normal)	1	1
Days per week (maximum)	5	5
Weeks per year	50	50
Emission per year (normal (lbs/year)	3.75	$5 \cdot 10^{-4}$
Emission per year (maximum) (lbs/year)	18.75	$1.3 \cdot 10^{-3}$

Depending on which process is implemented in each room, three possible "maximum" scenarios are possible (see table 5). The amount of fumes of H_2SO_4 and H_3PO_4 released is negligible in all cases.

Table 5. Maximum emission scenarios

Pollutant	NO_2	HF	HNO_3
Both BCP (lbs/year)	3600	75	115
Both EP (lbs/year)	-	37.5	-
BCP + EP (lbs/year)	1800	56.3	57.5

Clearly the scenario with the two cycles of BCP daily (one in each room) provides the maximum amount of pollutants, but most probably, this attractive from our view point scenario is less probable to happen.